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Two New Titanium Pyroarsenates:

α -TiAs₂O₇ and β -TiAs₂O₇.

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ABSTRACT. — Two new titanium pyroarsenate phases, α - TiAs_2O_7 and β - TiAs_2O_7 , have been prepared by high-temperature hydrothermal methods and characterized by single crystal X-ray diffraction techniques. Both structures are based on different three-dimensional networks of vertex-sharing TiO_6 octahedra and AsO_4 tetrahedra. The TiO_6 groups show little distortion from regular octahedral geometry and the arsenate anions are linked in pairs via As-O-As bonds to form pyroarsenate (As_2O_7) groups. α - TiAs_2O_7 is isostructural with a polymorph of SiP_2O_7 ; β - TiAs_2O_7 is a new structure.

Crystal data: α - TiAs_2O_7 : monoclinic, space group $P2_1/n$ (No. 14), with $a = 5.0992(8) \text{ \AA}$, $b = 12.879(3) \text{ \AA}$, $c = 8.219(2) \text{ \AA}$, $\alpha = 90^\circ$, $\beta = 91.313(4)^\circ$, $\gamma = 90^\circ$, $Z = 4$, $V = 539.62 \text{ \AA}^3$, $\rho_{\text{calc}} = 3.82 \text{ g/cm}^3$, 1712 observed reflections [$I > 3\sigma(I)$], $R = 6.47\%$ and $R_w = 7.14\%$.

β - TiAs_2O_7 : monoclinic, space group $C2/c$ (No. 15), with $a = 6.8697(7) \text{ \AA}$, $b = 7.9239(6) \text{ \AA}$, $c = 9.4369(8) \text{ \AA}$, $\alpha = 90^\circ$, $\beta = 104.072(4)^\circ$, $\gamma = 90^\circ$, $Z = 4$, $V = 498.28 \text{ \AA}^3$, $\rho_{\text{calc}} = 4.13 \text{ g/cm}^3$, 880 observed reflections [$I > 3\sigma(I)$], $R = 3.43\%$, $R_w = 4.13\%$.

INTRODUCTION

Many titanium/phosphate-containing materials, including such technologically-important phases as KTP (KTiOPO_4), have been characterized to various extents. KTP and its many isomorphs are of interest for their exceptional non-linear optical properties [1]. Although KTiOAsO_4 [2], the As-containing analogue of KTP, has been prepared, much less is known about other materials in the titanium/arsenate phase space [3]. This paper reports the results of our exploratory synthesis by high-temperature/high-pressure hydrothermal methods and single crystal X-ray structural characterization of two titanium pyroarsenate phases, $\alpha\text{-TiAs}_2\text{O}_7$ and $\beta\text{-TiAs}_2\text{O}_7$.

EXPERIMENTAL

Both of the title materials were prepared in the same hydrothermal reaction: 0.0809 g of TiO_2 , 2.34 g of $\text{As}_2\text{O}_5 \cdot n\text{H}_2\text{O}$ and 0.34 cm^3 of distilled water were sealed in a gold tube, dimensions $\frac{1}{4}'' \times 2\frac{1}{4}''$. This tube was placed in a LECO Tem-Pres high-pressure furnace, and thermally treated as follows: from room temperature, heat to 700°C over a 1 hour period (estimated $P_{\text{max}} = 60\,000 \text{ psi}$); cool to 650°C over 40 hours; cool to 350°C over 36 hours; switch off and cool to ambient (overnight). The tube was broken open and the solid product recovered from the mother liquor ($\text{pH} = 1$) by suction filtration. A mass of transparent crystals, with sizes up to 2 mm, were recovered, including a few rods, many equiaxial chunks, and other morphologies. The crystals from this reaction are stable in air for an indefinite period.

Suitable single crystals of $\alpha\text{-TiAs}_2\text{O}_7$ and $\beta\text{-TiAs}_2\text{O}_7$ for structure determination were selected and mounted on thin glass fibers with cyanoacrylate glue. Intensity data were collected at room-temperature [$25(2)^\circ\text{C}$] for each phase using a Huber automated 4-circle diffractometer (graphite-monochromated $\text{MoK}\alpha$ radiation, $\lambda = 0.71073 \text{ \AA}$) as outlined in Table I, by procedures fully described elsewhere [4]. After successful structure solution, the centrosymmetric space group C2/c was assumed in all subsequent crystallographic analysis of $\beta\text{-TiAs}_2\text{O}_7$.

Starting positions for the heavy atoms (Ti and As) were obtained by direct-methods using the program SHELXS-86 [5] in each case, and the oxygen

TABLE I: Crystallographic Parameters

	α -TiAs ₂ O ₇	β -TiAs ₂ O ₇
emp. formula	As ₂ TiO ₇	As ₂ TiO ₇
mol wt.	309.74	309.74
habit	colorless shard	colorless lump
crystal size (mm)	0.6 × 0.1 × 0.05	0.4 × 0.4 × 0.3
crystal system	monoclinic	monoclinic
a (Å)	5.092(8)	6.8697(7)
b (Å)	12.879(3)	7.9239(6)
c (Å)	8.219(2)	9.4369(8)
β (°)	91.313(4)	104.072(4)
V (Å ³)	539.62	498.28
Z	4	4
systematic absences	h0l, h+l; 0k0, k	hkl, h+k; h0l, h,l; 0k0, k
space group	P2 ₁ /n (No. 14)	C2/c (No. 15)
T (°C)	25(2)	25(2)
λ (Mo K α) (Å)	0.71073	0.71073
ρ_{calc} (g/cm ³)	3.81	4.13
μ (cm ⁻¹)	137.0	148.3
absorption correction	DIFABS [17]	ψ -scans
extinction parameter	110(9)	124(6)
hkl-limits	±7,+19,+12	±10,+11,+14
total data	2233	2011
observed data§	1712	880
parameters	92	49
R(F _o) ^a (%)	6.47	3.43
R _w (F _o) ^b (%)	7.14	4.13

§ $I > 3\sigma(I)$

$$R^a = \Sigma ||F_o| - |F_c||/|F_o|, R_w^b = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$$

atoms were located from Fourier difference maps following refinement of the heavy-atom positions (refinement software: CRYSTALS [6]). No particular problems were encountered during the refinements, and tables of anisotropic thermal factors and observed and calculated structure factors are available from the authors.

RESULTS

A. α -Titanium Pyroarsenate, α -TiAs₂O₇

Final atomic positional and thermal parameters for α titanium pyroarsenate, α -TiAs₂O₇, are listed in Table II, with selected bond distance/angle data in Table III. This new phase (Figure 1) consists of a three-dimensional network of octahedral TiO₆ groups and pairs of tetrahedral AsO₄ groups, linked together via Ti-O-As and As-O-As bonds, the latter linkage leading to pyroarsenate (As₂O₇) units.

TABLE II: Atomic Positional Parameters for α -TiAs₂O₇

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{eq} *
Ti(1)	-0.2963 (2)	0.34590 (7)	0.3467 (1)	0.0100
As(1)	0.2044 (1)	0.18862 (4)	0.44008 (6)	0.0096
As(2)	-0.1869 (1)	0.48443 (4)	0.69056 (6)	0.0095
O(1)	0.0029 (8)	0.2569 (3)	0.3210 (5)	0.0134
O(2)	-0.4105 (8)	0.3206 (3)	0.1273 (5)	0.0131
O(3)	-0.1612 (9)	0.3835 (3)	0.5648 (5)	0.0151
O(4)	-0.6049 (8)	0.4271 (3)	0.3811 (5)	0.0139
O(5)	-0.4834 (8)	0.2246 (3)	0.4276 (5)	0.0155
O(6)	-0.1047 (9)	0.4654 (3)	0.2580 (5)	0.0159
O(7)	0.1840 (8)	0.0612 (3)	0.3694 (5)	0.0141

$$*U_{eq}(\text{\AA}^2) = (U_1 U_2 U_3)^{1/3}$$

α -TiAs₂O₇ contains 10 species in the asymmetric unit—1 Ti atom, 2 As atoms and 7 O atoms. The titanium atom bonds to 6 of the 7 oxygen atoms, all of which bridge to an adjacent As-atom center. Each As atom makes 3 As-O-Ti links and its remaining vertex [O(7)] is the bridging oxygen atom of

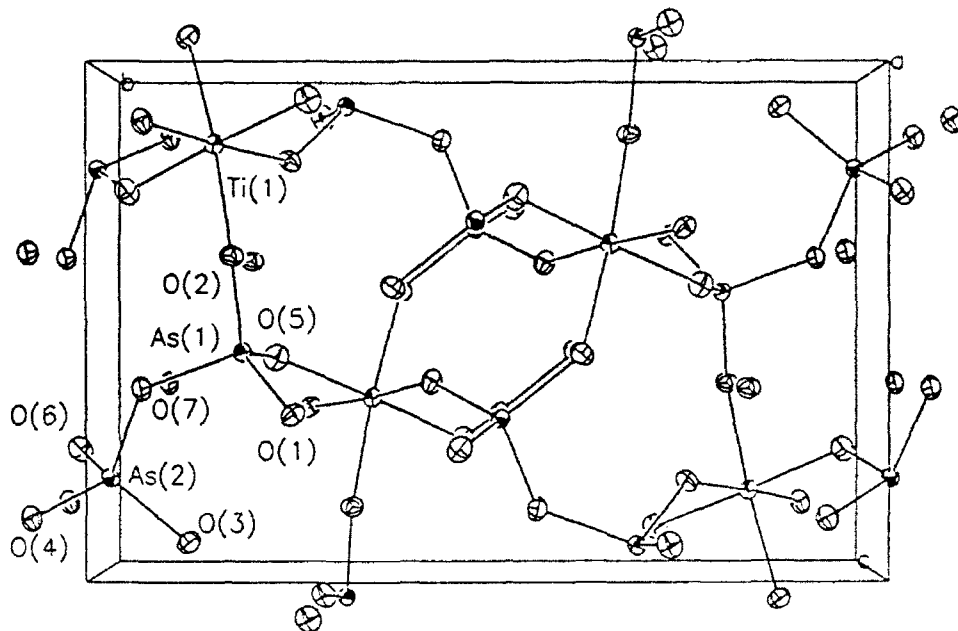


Figure 1: ORTEP [15] view of the crystal structure of α - TiAs_2O_7 , viewed down $[100]$. Thermal ellipsoids are drawn at the 50% level.

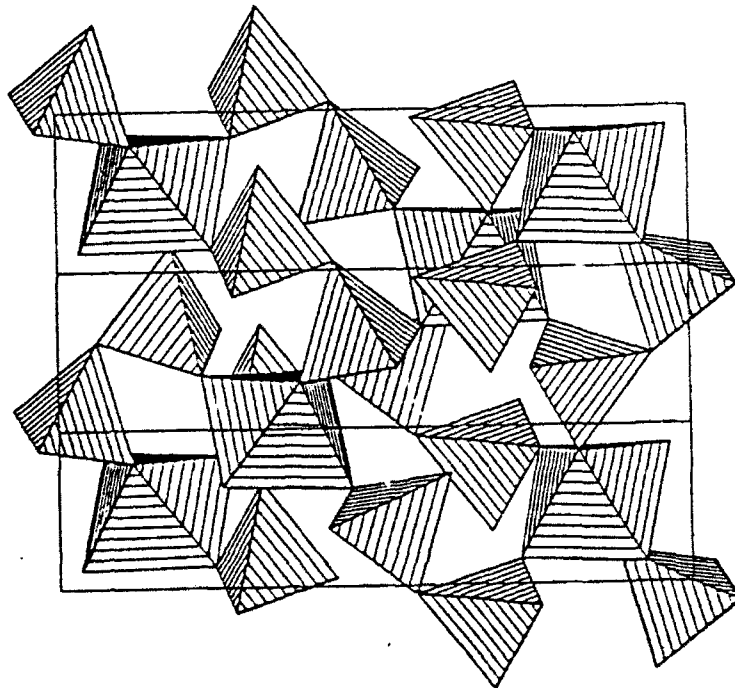


Figure 2: Polyhedral plot (STRUPLO: [16]) of the crystal structure of α - TiAs_2O_7 , viewed down $[201]$.

the pyroarsenate group. The Ti-O distances are typical [$d_{av} = 1.942(2) \text{ \AA}$] and there is no distinct, short, "titanyl" Ti=O bond [$d(\text{Ti}-\text{O}) < 1.75 \text{ \AA}$], as is found for octahedral Ti^{4+} in KTiOAsO_4 [2] and similar phases. The six As-O bonds which link to titanium atoms are also characteristic [$d_{av} = 1.662(2) \text{ \AA}$], and the average Ti-O-As bond angle is $138.3(1)^\circ$. The As-O bonds in the pyroarsenate linkage are somewhat lengthened [$d_{av} = 1.735(3) \text{ \AA}$] compared to the As-O bonds in the As-O-Ti links, akin to the extended P-O bonds in the P-O-P bridge in pyrophosphate species [7].

TABLE III: Bond Distances (\AA) and Angles ($^\circ$) for $\alpha\text{-TiAs}_2\text{O}_7$

Ti(1)-O(1)	1.924(4)	Ti(1)-O(2)	1.910(4)
Ti(1)-O(3)	1.966(4)	Ti(1)-O(4)	1.916(4)
Ti(1)-O(5)	1.955(4)	Ti(1)-O(6)	1.971(4)
As(1)-O(1)	1.655(4)	As(1)-O(2)	1.663(4)
As(1)-O(5)	1.663(4)	As(1)-O(7)	1.743(4)
As(2)-O(3)	1.668(4)	As(2)-O(4)	1.656(4)
As(2)-O(6)	1.667(4)	As(2)-O(7)	1.727(4)
O(2)-Ti(1)-O(1)	91.1(2)	O(3)-Ti(1)-O(1)	89.1(2)
O(3)-Ti(1)-O(2)	174.6(2)	O(4)-Ti(1)-O(1)	176.0(2)
O(4)-Ti(1)-O(2)	89.9(2)	O(4)-Ti(1)-O(3)	90.2(2)
O(5)-Ti(1)-O(1)	87.4(2)	O(5)-Ti(1)-O(2)	92.5(2)
O(5)-Ti(1)-O(3)	92.9(2)	O(5)-Ti(1)-O(4)	88.7(2)
O(6)-Ti(1)-O(1)	91.4(2)	O(6)-Ti(1)-O(2)	85.8(2)
O(6)-Ti(1)-O(3)	88.8(2)	O(6)-Ti(1)-O(4)	92.5(2)
O(6)-Ti(1)-O(5)	177.9(2)	O(2)-As(1)-O(1)	111.0(2)
O(5)-As(1)-O(1)	113.5(2)	O(5)-As(1)-O(2)	115.8(2)
O(7)-As(1)-O(1)	105.8(2)	O(7)-As(1)-O(2)	102.8(2)
O(7)-As(1)-O(5)	106.9(2)	O(4)-As(2)-O(3)	112.0(2)
O(6)-As(2)-O(3)	112.2(2)	O(6)-As(2)-O(4)	112.6(2)
O(7)-As(2)-O(3)	107.4(2)	O(7)-As(2)-O(4)	106.4(2)
O(7)-As(2)-O(6)	105.7(2)	As(1)-O(1)-Ti(1)	137.3(2)
As(1)-O(2)-Ti(1)	141.2(3)	As(2)-O(3)-Ti(1)	136.5(2)
As(2)-O(4)-Ti(1)	147.7(3)	As(1)-O(5)-Ti(1)	135.9(2)
As(2)-O(6)-Ti(1)	131.0(2)	As(2)-O(7)-As(1)	125.6(2)

This Ti/As/O connectivity leads to the polyhedral networks illustrated in

Figure 2: interleaved layers of vertex-sharing TiO_6 and As_2O_7 groups are roughly aligned in the ac -plane. The smallest identifiable atomic-connectivity "loops" include $-\text{Ti}-\text{As}-\text{Ti}-\text{As}-$ "4-rings" and $-\text{Ti}-\text{As}-\text{As}-\text{Ti}-\text{As}-$ "5-rings" (linking O-atoms omitted). $\alpha\text{-TiAs}_2\text{O}_7$ has an interesting structural analogue in one of the polymorphs of SiP_2O_7 [8], which is one of the few crystal structures containing octahedrally-coordinated silicon atoms.

A. β -Titanium Pyroarsenate, $\beta\text{-TiAs}_2\text{O}_7$

Final atomic positional and thermal parameters with e.s.d.'s for β titanium pyroarsenate, $\beta\text{-TiAs}_2\text{O}_7$, are listed in Table IV, with selected geometrical data in Table V. This structure (Figure 3) is also built up from TiO_6 and As_2O_7 units, but the connectivity is different from that found in $\alpha\text{-TiAs}_2\text{O}_7$.

TABLE IV: Atomic Positional Parameters for $\beta\text{-TiAs}_2\text{O}_7$

Atom	x	y	z	U_{eq}^*
Ti(1)	0	0	0	0.0125
As(1)	0.30569 (7)	0.13280 (6)	-0.19848 (5)	0.0119
O(1)	1/2	0.0277 (6)	-1/4	0.0152
O(2)	0.2412 (5)	0.0075 (5)	-0.0763 (4)	0.0157
O(3)	0.1294 (5)	-0.1614 (5)	0.1472 (4)	0.0152
O(4)	0.1064 (6)	0.1811 (5)	0.1300 (4)	0.0178

$$*U_{eq}(\text{\AA}^2) = (U_1 U_2 U_3)^{1/3}$$

There are six asymmetric atoms (one octahedral Ti, one tetrahedral As, three Ti-O-As bridging-O, one As-O-As bridging-O), which all show their characteristic bonding geometries: $d_{av}(\text{Ti}-\text{O}) = 1.938(2) \text{\AA}$, $d_{av}(\text{As}-\text{O}_{\text{Ti}}) = 1.664(3) \text{\AA}$, $d(\text{As}-\text{O}_{\text{As}}) = 1.740(3) \text{\AA}$, $\theta_{av}(\text{Ti}-\text{O}-\text{As}) = 141.8(2)^\circ$. The Ti atom is located at an inversion center, and is in a very regular coordination environment; the pyroarsenate-group bridging oxygen atom, O(1), is located on a two-fold axis, and the other atoms occupy general crystallographic positions. Compared to $\alpha\text{-TiAs}_2\text{O}_7$, the most significant geometrical change is the expanded Ti(1)-O(4)-As(1) bond angle: the As-O-As angle is virtually unchanged in the two structures.

Figure 4 indicates the $\text{TiO}_6/\text{As}_2\text{O}_7$ polyhedral connectivity. Once again, interlinked sheets of Ti- and As-centered polyhedra may be identified, this

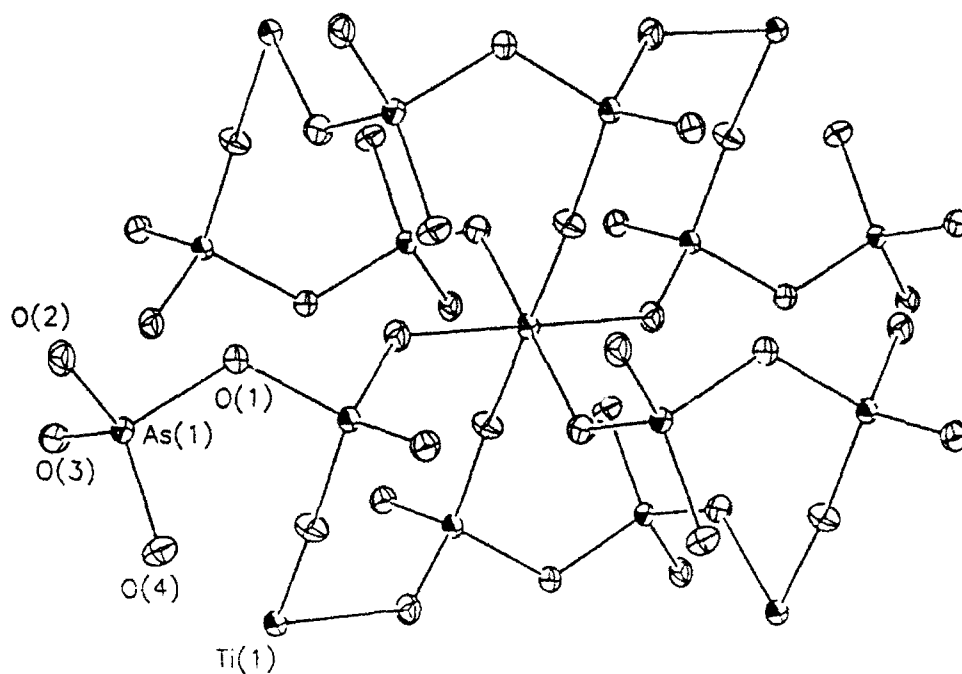


Figure 3: ORTEP view of an *ab*-slice of the crystal structure of β - TiAs_2O_7 , viewed down the *c*-direction. Thermal ellipsoids are drawn at the 50% level.

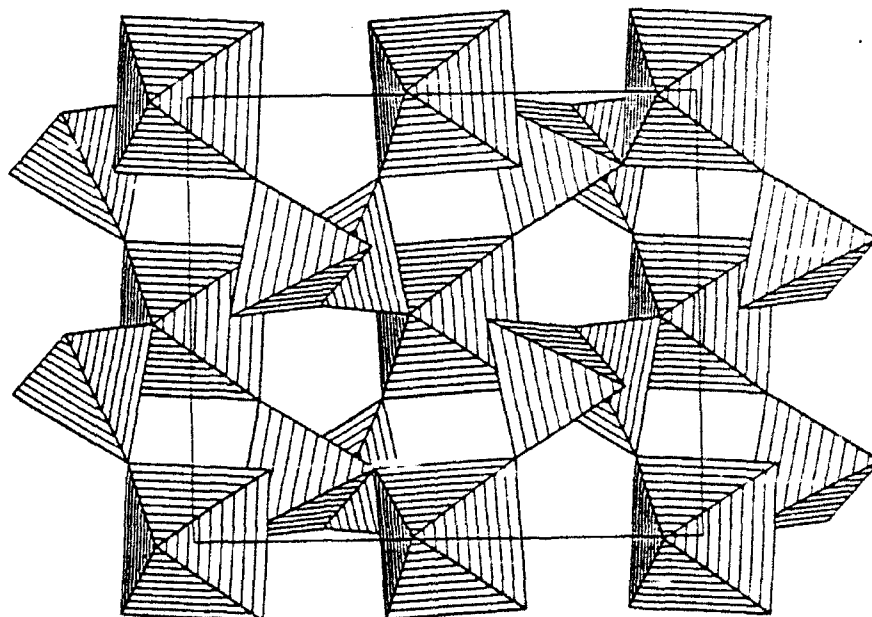


Figure 4: Polyhedral plot (STRUPLO) of the crystal structure of β - TiAs_2O_7 , viewed down [100].

time in the *ab*-plane. Similar 4- and 5-rings make up the Ti/As/O linkages.

TABLE V: Bond Distances (Å) and Angles (°) for β -TiAs₂O₇

Ti(1)-O(2)	1.962(3) × 2	Ti(1)-O(3)	1.938(4) × 2
Ti(1)-O(4)	1.914(4) × 2	As(1)-O(1)	1.740(3)
As(1)-O(2)	1.662(4)	As(1)-O(3)	1.668(4)
As(1)-O(4)	1.663(4)		
O(2)-Ti(1)-O(2)'	180 [‡]	O(3)-Ti(1)-O(2)	90.1(1)
O(3)-Ti(1)-O(2)	89.9(1)	O(3)-Ti(1)-O(3)'	180 [‡]
O(4)-Ti(1)-O(2)	89.3(2)	O(4)-Ti(1)-O(2)	90.7(2)
O(4)-Ti(1)-O(3)	89.9(2)	O(4)-Ti(1)-O(3)	90.1(2)
O(4)-Ti(1)-O(4)'	180 [‡]	O(2)-As(1)-O(1)	105.1(2)
O(3)-As(1)-O(1)	105.3(1)	O(3)-As(1)-O(2)	115.3(2)
O(4)-As(1)-O(1)	107.6(2)	O(4)-As(1)-O(2)	113.1(2)
O(4)-As(1)-O(3)	109.7(2)	As(1)-O(1)-As(1)'	122.8(3)
As(1)-O(2)-Ti(1)	131.6(2)	As(1)-O(3)-Ti(1)	130.2(2)
As(1)-O(4)-Ti(1)	163.7(3)		

[‡]by symmetry

DISCUSSION

Two new titanium pyroarsenates, α -TiAs₂O₇ and β -TiAs₂O₇, have been prepared and structurally characterized. Their octahedral/tetrahedral networks may be rationalized in terms of the typical crystallochemical behavior of their component species. The unit-cell volumes and densities of these two phases differ by about 8% (β -TiAs₂O₇ more dense than α -TiAs₂O₇), suggesting that β -TiAs₂O₇ might be the stable form of titanium pyroarsenate at higher pressures. Of course, many materials, including zirconium pyrophosphate, ZrP₂O₇ [9], and silicon pyrophosphate, SiP₂O₇ [10], show such polymorphism, but the co-synthesis of the two Ti/As/O polymorphs in one reaction is a typical feature of the non-equilibrium conditions often present in hydrothermal reactions.

Neither material reported here is isomorphous with any titanium pyrophosphate phases, or other M^{IV} As₂O₇ types. The M^{IV} P₂O₇ family has been quite

extensively studied [7,11] and a number of related phases reported: $M = \text{Hf, Ge, Np, Zr, Sn, Si, U, Th, Ti, Re, Pb, Ce}$. These are probably all based on a large ($a = \sim 22\text{--}23 \text{ \AA}$) cubic cell [12], whereas earlier work indicated a $a/3$ subcell, which would require the presence of linear P-O-P bridging links in the pyrophosphate group. The few characterized $M^{\text{IV}}\text{As}_2\text{O}_7$ -type phases ($M = \text{Zr, Th, Np}$) are apparently isomorphs of the cubic $M^{\text{IV}}\text{P}_2\text{O}_7$ phase [11].

Both materials reported here are notable for the regularity of the TiO_6 octahedral grouping. The distortion of the TiO_6 group in KTP has recently been discussed in terms of a molecular-orbital model, in which O-Ti-O bond distortion is viewed in terms of orbital mixing as the TiO_6 geometry changes [13]. The resulting TiO_6 configuration reflects the competition between the stabilization gained by the distortion versus the destabilizing effect on other occupied molecular orbitals. In both $\alpha\text{-TiAs}_2\text{O}_7$ and $\beta\text{-TiAs}_2\text{O}_7$, all six Ti-O vertices connect to an As center, thus, it appears that any additional stability which the TiO_6 octahedron might attain on distortion is offset by the destabilizing effect on the As_2O_7 group, and the TiO_6 moiety is essentially regular. We have also noticed that in materials containing dimeric Ti_2O_{11} and trimeric Ti_3O_{16} groupings [14], the Ti-O distortion is greatly reduced compared to that found in KTP-type materials.

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REFERENCES

- [1] G. D. Stucky, M. L. F. Phillips and T. E. Gier. *Chem. Mater.* 1989, 1, 492.
- [2] M. El Brahimi and J. Durand. *Rev. Chim. Mineral.* 1986, 23, 146.
- [3] N. G. Chernorukov, I. A. Korshunov and M. I. Zhuk. *Russ. J. Inorg. Chem.* 1982, 27, 1728.

- [4] W. T. A. Harrison, T. E. Martin, T. E. Gier and G. D. Stucky. *J. Mater. Chem.* 1992, **2**, 175.
- [5] G. M. Sheldrick. *SHELXS-86 User Guide*, Crystallography Department, University of Göttingen, Germany, 1986.
- [6] D. J. Watkin, J. R. Carruthers and P. W. Betteridge. *CRYSTALS User Guide*, Chemical Crystallography Laboratory, Oxford University, UK, 1985.
- [7] A. F. Wells. "Structural Inorganic Chemistry", Fifth edition, Oxford, 1986, p 859.
- [8] K.-F. Hesse. *Acta Crystallogr.* 1979, **B35**, 724.
- [9] M. Chaunac. *Bull. Soc. Chim. France.* 1971, 424.
- [10] H. Makart. *Helv. Chim. Acta* 1967, **50**, 399.
- [11] Data from the JCPDS Powder Diffraction File, 1991 version.
- [12] E. Tillmanns, W. Gebert and W. M. Meier. *J. Sol. St. Chem.* 1973, **7**, 69.
- [13] M. L. F. Phillips, W. T. A. Harrison, T. E. Gier, G. D. Stucky, G. V. Kulkarni and J. K. Burdett. *Inorg. Chem.* 1990, **29**, 2158.
- [14] W. T. A. Harrison, T. E. Gier, J. C. Calabrese, A. Monnier and G. D. Stucky, *Chem. Mater.* 1993, submitted.
- [15] C. K. Johnson. Report ORNL-5138, Oak Ridge National Laboratory, Tennessee, USA, 1976.
- [16] R. X. Fischer. *J. Appl. Crystallogr.* 1985, **18**, 258.
- [17] N. Walker and J. Stuart. *Acta Crystallogr.* 1983, **A39**, 158.

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